1 536 429

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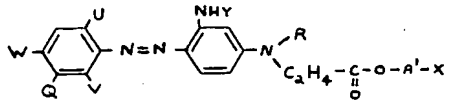
(19)

(54) DISPERSE MONOAZO DYESTUFFS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to disperse monoazo dyestuffs which are valuable for colouring synthetic textile materials, in particular aromatic polyester textile materials.

In British Application No. 26808/72 (Ser. No. 1,413,322) there are described and claimed the disperse monoazo dyestuffs of the formula:—



wherein U is hydrogen, chlorine, bromine, cyano, lower alkyl, lower alkoxy or a group of the formula —$CONT^1T^2$, —$COOT^3$ or —SO_2T^3;

V is hydogen, chlorine, bromine, cyano or lower alkoxycarbonyl;

W is hydrogen, cyano, nitro, thiocyano, chlorine, bromine or a group of the formula —$SO_2NT^1T^2$, —$COOT^3$ or —SO_2T^3;

Q is hydrogen, chlorine, bromine, lower alkoxy or a —$COOT^3$ group;

R is cyano lower alkyl;

A^1 represents a lower alkylene radical;

X is cyano, lower alkoxy, lower alkoxy lower alkoxy, lower alkoxy lower alkoxy lower alkoxy, chlorine, bromine, lower alkoxycarbonyl, lower alkycarbonyl, optionally substituted phenoxy carbonyl or optionally substituted phenoxy;

Y is lower alkoxycarbonyl, lower alkylcarbonyl, optionally substituted phenylcarbonyl, optionally substituted phenoxycarbonyl, phenyl lower alkoxycarbonyl, lower alkylsulphonyl, optionally substituted phenylsulphonyl or N-optionally substituted aminocarbonyl;

T^1 is hydrogen or alkyl;

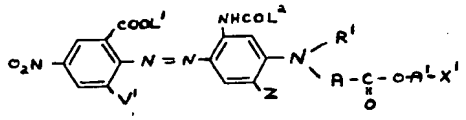
T^2 is hydrogen, alkyl, phenyl, phenylalkyl or cycloalkyl;

and T^3 is alkyl, phenyl, phenylalkyl or cycloalkyl.

The said Application also describes and claims a process for the manufacture of the said dyestuffs and their use for colouring synthetic textile materials.

It has now been found that the dyestuffs of the above formula wherein U is lower alkoxycarbonyl, W is nitro, Q is hydrogen and V is hydrogen or nitro are particularly valuable for colouring aromatic polyester textile materials as, when such dystuffs are applied by aqueous colouration processes, any unfixed dyestuff on the surface of the textile material can be readily removed by treatment in a warm aqueous solution of an alkali which does not contain a reducing agent (such as sodium hydrosulphite).

According to the present invention, there are provided the disperse monoazo dyestuffs of the formula:—



wherein

L^1 represnts optionally substituted lower alkyl;

L^2 represents optionally substituted lower alkyl or optionally substituted amino,

V^1 is hydrogen or nitro;

Z is hydrogen or lower alkoxy;

R^1 is lower alkyl or cyano lower alkyl;

A and A^1 each independently represent lower alkylene; and

X^1 is cyano, lower alkoxy, lower alkoxy lower alkoxy, lower alkoxy lower alkoxy lower alkoxy, chlorine, bromine, lower alkoxycarbonyl, lower alkylcarbonyl, optionally substituted phenoxycarbonyl, optionally substituted phenylcarbonyl, optionally substituted phenoxy, hydroxymethyl or lower alkyl carbonyloxymethyl.

Throughout this Specification the terms "lower alkyl" "lower alkoxy" and "lower alkylene" are used to denote alkyl, alkoxy and alkylene radicals respectively containing from 1 to 4 carbon atoms.

As examples of the lower alkylene radicals represented by A and A^1 there may be mentioned methylene, trimethylene, tetramethylene, propylene and, above all, ethylene. As examples of the cyano lower alkyl radicals represented by R^1 there may be mentioned cyanomethyl, γ-cyanopropyl, δ-cyanobutyl and, above all, β-cyanoethyl. As examples of the lower alkyl radicals represented by L^1, L^2 and R^1 there may be mentioned methyl, ethyl, *n*-propyl and *n*-butyl. As examples of lower alkoxy represented by Z there may be mentioned ethoxy and, preferably, methoxy.

As examples of substituted lower alkyl radicals represented by L^1 and L^2 there may be mentioned hydroxy lower alkyl such as β-hydroxyethyl, chloro lower alkyl such as β-chloroethyl, cyano lower alkyl such as β-cyanoethyl, lower alkoxy lower alkyl such as β-ethoxyethyl and γ-methoxypropyl, phenyl lower alkyl such as benzyl and β-phenylethyl, and phenoxy lower alkyl such as phenoxymethyl.

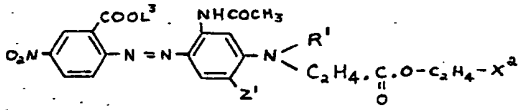
As examples of the substituted amino groups represented by L^2 there may be mentioned lower alkylamino such as methylamino and ethylamino.

It is however preferred that L^1 is lower alkyl. It is also preferred that L^2 is lower alkyl, in particular methyl.

As specific examples of the groups represented by X^1 there may be mentioned lower alkoxy such as methoxy, ethoxy, *n*-propoxy and *n*-butoxy, lower alkoxy lower alkoxy such as β-ethoxyethoxy and γ-methoxypropoxy, lower alkoxy lower alkoxy lower alkoxy such as β-(β'-methoxyethoxy)ethoxy, lower alkoxycarbonyl such as methoxycarbonyl, ethoxycarbonyl and *n*-butoxycarbonyl, lower alkylcarbonyl such as acetyl and propionyl, optionally substituted phenoxycarbonyl such as phenoxycarbonyl itself, *p*-methylphenoxycarbonyl and *m*-chlorophenoxycarbonyl, optionally substituted phenylcarbonyl such as benzoyl and *m*-nitrobenzyl, optionally substituted phenoxy such as phenoxy itself, tolyloxy and chlorophenoxy, and lower alkylcarbonyloxymethyl such as acetoxymethyl.

It is however preferred that X^1 is cyano, lower alkoxy, lower alkoxy lower alkoxy, lower alkoxycarbonyl, lower alkylcarbonyl, hydroxymethyl or lower alkylcarbonyloxymethyl.

A preferred class of the dyestuffs of the invention comprises the dyestuffs of the formula:—



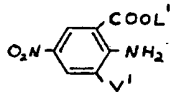
wherein R^1 has the meaning stated;

L^3 is lower alkyl

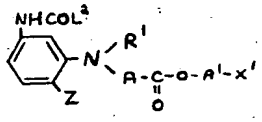
Z^1 is hydrogen or methoxy; and

X^2 is cyano, lower alkoxy, lower alkoxy lower alkoxy, lower alkoxycarbonyl, lower alkylcarbonyl, hydroxymethyl or lower alkylcarbonyloxy methyl.

The dyestuffs of the present invention can be obtained by a similar method to that described and claimed in British Application No. 26808/72 (Serial No. 1,413,322) and comprises diazotising an amine of the formula:—



and coupling the resulting diazo compound with a coupling component of the formula:—



wherein A, A^1, L^1, L^2, R^1, V^1, X^1 and Z have the meanings stated.

As specific examples of the said amines there may be mentioned the methyl, ethyl, *n*-propyl, *iso*-propyl, isobutyl, *sec*-butyl and *n*-butyl esters of 2-amino-5-nitrobenzoic acid and of 2-amino-3:5-dinitrobenzoic acid.

As specific examples of the said coupling components there may be mentioned 2-(methoxy or ethoxy)-5-acetylamino-N-(methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl or β-cyanoethyl)-N-[β-(β'-[cyano, methoxy, ethoxy or phenoxy]ethoxycarbonyl)ethyl]aniline, 3-acetylamino-N-(methyl, ethyl, *n*-butyl, cyanomethyl, cyanopropyl, cyanobutyl or β-cyanoethyl)-N-[β-(β'-[cyano, methoxy, methoxy, ethoxy or phenoxy]ethoxycarbonyl)ethyl]aniline, 3-(acetylamino, propionylamino, *n*- or iso-butyrylamino)-N-(methyl, ethyl or β-cyanoethyl)-N-[β-(β'-[chloro, bromo, methoxycarbonyl, acetyl, benzoyl, phenoxycarbonyl, hydroxymethyl or acetoxymethyl]ethoxycarbonyl)ethyl]aniline and 3-(acetylamino or propionylamino)-N-(methyl, ethyl or β-cyanoethyl)-N-[β-[β(β'-[β''-methoxyethoxy]ethoxycarbonyl)ethyl]aniline.

The azo dyestuffs of the present invention are valuable for colouring synthetic textile materials, in particular aromatic polyester textile materials, by aqueous dyeing, padding or printing processes using the techniques which are conventionally employed in colouring synthetic textile materials. The said dyestuffs are particularly valuable for colouring aromatic polyester textile materials as any unfixed dyestuff can readily be removed from the surface of the textile material by treatment for a few minutes in a warm aqueous solution of an alkali, such as an aqueous solution of sodium carbonate, of pH in the range of 8 to 12. The resulting scarlet to blue colourations have excellent fastness to the tests conventionally applied to such textile materials.

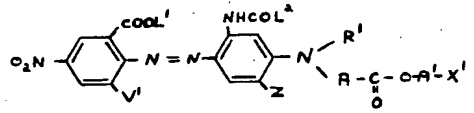
The invention is illustrated but not limited by the following Examples in which the parts and percentages are by weight.

Example 1.

A solution of 3.92 parts of methyl 2-amino-5-nitrobenzoate in a mixture of 60 parts of acetic acid and 5 parts of a concentrated aqueous solution of hydrochloric acid is cooled to 5°—10°C, 12 parts of a 14% aqueous soluton of sodium nitrite are added, and the mixture stirred for 10 minutes at 5°—10°C. The resulting solution of the diazo compound is added to a stirred mixture of 6.66 parts of 3-acetylamino-N-(β-cyanoethyl)-N-[β-(β'-methoxyethoxycarbonyl)ethyl]aniline, 500 parts of water and 10 parts of acetone at 0°—10°C, sodium acetate is added until the mixture is no longer acid to Congo Red, and the mixture is stirred for 4 hours at 5°C. The precipitated dyestuff is then filtered off, washed with water and dried.

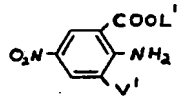
An aqueous dispersion of the dyestuff is prepared in conventional manner, and the resulting dispersion is then incorporated into a print paste which is applied to a woven aromatic polyester textile material after which the textile material is dried and then steamed to fix the dyestuff. The printed textile material is then treated in a warm aqueous solution of sodium of sodium carbonate of pH 11 to remove any unfixed dyestuff from the surface of the textile material, and the print is then rinsed in water and dried. A bright red print is obtained which has excellent fastness to light, to rubbing and to wet and to dry heat treatments.

The following Table gives further Examples of the dyestuffs of the invention of the formula:—

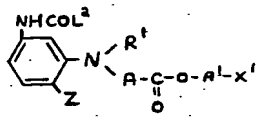


the symbols of which have the values given in the respective columns of the Table, the shades obtained when the said dyestuffs are applied to an aromatic polyester textile material being given in the last column of the Table.

These dyestuffs were obtained by diazotising the appropriate amine of the formula:—



and coupling the resulting diazo compound with the approprate coupling component of the formula:—



Example	L^1	V^1	L^2	Z	R^1	A	A^1	X^1	Shade
2	methyl	hydrogen	methyl	methoxy	ethyl	ethylene	ethylene	methoxy	Violet
3	,,	,,	,,	ethoxy	,,	,,	,,	,,	,,
4	,,	,,	,,	hydrogen	β-cyanoethyl	,,	methylene	cyano	Red
5	,,	,,	,,	,,	cyanomethyl	,,	ethylene	β-methoxy-ethoxy	Scarlet
6	,,	,,	,,	,,	γ-cyanopropyl	,,	,,	,,	Bluish-red
7	,,	,,	β-chloro-	,,	β-cyanoethyl	trimethylene	,,	*n*-butoxy	Red
8	,,	,,	ethyl	,,	,,	ethylene	trimethylene	methoxy	,,
9	,,	,,	methyl	,,	,,	trimethylene	methylene	cyano	,,
10	,,	,,	amino	,,	,,	β-methyl-ethylene	ethylene	methoxy	,,
11	,,	,,	methyl	,,	γ-cyanopropyl	ethylene	trimethylene	phenoxy	Bluish-red
12	,,	,,	ethyl	,,	β-cyanoethyl	,,	ethylene	bromine	Red
13	,,	,,	methyl	,,	,,	,,	,,	chlorine	,,
14	,,	,,	,,	,,	,,	,,	,,	methoxy - carbonyl	,,
15	,,	,,	,,	,,	,,	,,	tetramethylene	methoxy	,,
16	,,	,,	,,	,,	s-cyanobutyl	,,	ethylene	,,	Rubine
17	,,	,,	,,	,,	β-cyanoethyl	,,	,,	phenoxy-carbonyl	Red
18	,,	,,	,,	,,	,,	,,	methylene	benzoyl	,,

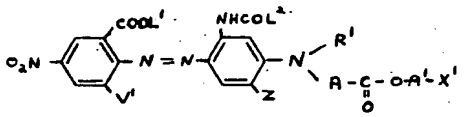
Example	L^1	V^1	L^2	Z	R^1	A	A^1	X^1	Shade
19	methyl	hydrogen	*n*-butyl	hydrogen	β-cyanoethyl	ethylene	methylene	acetyl	Red
20	,,	,,	methyl	,,	ethyl	,,	,,	,,	Rubine
21	,,	,,	,,	,,	β-cyanoethyl	,,	ethylene	ethoxy	Red
22	,,	,,	,,	,,	,,	,,	,,	β-(β'-methoxy-ethoxy)ethoxy	,,
23	,,	,,	,,	,,	,,	,,	,,	cyano	,,
24	,,	,,	ethylamino	,,	,,	,,	,,	methoxy	,,
25	,,	,,	methyl	,,	methyl	,,	,,	,,	Bluish-red
26	,,	,,	,,	,,	ethyl	ethylene	,,	,,	Rubine
27	,,	,,	,,	,,	*n*-propyl	,,	,,	,,	,,
28	,,	,,	,,	,,	*n*-butyl	,,	,,	,,	,,
29	,,	,,	,,	,,	ethyl	,,	methylene	cyano	,,
30	,,	,,	,,	,,	,,	,,	ethylene	β-methoxy-ethoxy	,,
31	,,	,,	,,	,,	,,	,,	methylene	methoxy-carbonyl	,,
32	,,	,,	,,	,,	,,	,,	,,	ethoxycarbonyl	,,
33	,,	,,	,,	,,	,,	,,	,,	acetyl	,,
34	,,	,,	,,	methoxy	β-cyanoethyl	,,	ethylene	methoxy	,,
35	,,	,,	,,	ethoxy	,,	,,	,,	,,	,,

Example	L^1	V^1	L^2	Z	R^1	A	A^1	X^1	Shade
36	methyl	hydrogen	methyl	methoxy	ethyl	ethylene	methylene	cyano	Rubine
37	,,	,,	,,	,,	,,	,,	ethylene	β-methoxy-ethoxy	,,
38	,,	,,	,,	,,	,,	,,	methylene	methoxycarbonyl	,,
39	,,	,,	,,	,,	,,	,,	,,	acetyl	,,
40	ethyl	,,	,,	hydrogen	β-cyanoethyl	,,	ethylene	methoxy	Red
41	,,	,,	,,	methoxy	,,	,,	,,	,,	Rubine
42	,,	,,	,,	,,	ethyl	,,	,,	,,	Violet
43	*n*-propyl	,,	,,	hydrogen	β-cyanoethyl	,,	,,	,,	Red
44	*n*-butyl	,,	,,	,,	,,	,,	,,	,,	,,
45	methyl	,,	,,	,,	,,	,,	methylene	hydroxymethyl	,,
46	,,	,,	,,	,,	ethyl	,,	,,	,,	Rubine
47	,,	,,	,,	ethoxy	β-cyanoethyl	,,	,,	,,	,,
48	,,	,,	,,	methoxy	ethyl	,,	,,	,,	,,
49	,,	,,	,,	hydrogen	β-cyanoethyl	,,	,,	acetyloxymethyl	Red
50	,,	,,	,,	methoxy	ethyl	,,	,,	,,	Violet
51	methyl	,,	methyl	hydrogen	β-cyanoethyl	ethylene	ethylene	hydroxymethyl	Red
52	,,	,,	benzyl	,,	,,	,,	,,	methoxy	,,
53	,,	,,	phenoxy-methyl	,,	,,	,,	,,	,,	,,

Example	L^1	V^1	L^2	Z	R^1	A	A^1	X^1	Shade
54	methyl	hydrogen	methyl	methoxy	ethyl	ethylene	methylene	ethoxycarbonyl	Violet
55	,,	,,	,,	ethoxy	,,	,,	,,	acetyl	,,
56	,,	,,	,,	,,	,,	,,	,,	propionyloxy-methyl	,,
57	,,	,,	,,	hydrogen	β-cyanoethyl	,,	,,	propylcarbonyl-oxy methyl	Red
58	β-methoxy ethoxy	,,	,,	,,	,,	,,	,,	methoxy	,,
59	β-chloro ethyl	,,	,,	,,	,,	,,	,,	,,	,,
60	β-cyano ethyl	,,	,,	,,	,,	,,	,,	,,	,,
61	methyl	nitro	,,	,,	,,	,,	,,	,,	,,
62	ethyl	,,	,,	,,	,,	,,	,,	,,	,,
63	isopropyl	hydrogen	,,	,,	,,	,,	,,	,,	,,
64	β-methyl-*n*-propyl	,,	,,	,,	,,	,,	,,	,,	,,
65	α-methyl-*n*-propyl	,,	,,	,,	,,	,,	,,	,,	,,
66	methyl	nitro	,,	methoxy	,,	,,	,,	,,	Reddish-blue
67	,,	,,	,,	hydrogen	ethyl	,,	,,	,,	Violet
68	,,	,,	,,	methoxy	,,	,,	,,	,,	Greenish-blue
69	,,	,,	,,	hydrogen	cyanoethyl	,,	methylene	hydroxymethyl	Rubine
70	,,	,,	,,	methoxy	ethyl	,,	,,	,,	Greenish-blue

WHAT WE CLAIM IS:—

1. Disperse monoazo dyestuffs of the formula:—



wherein

L^1 represents optionally substituted lower alkyl;

L^2 represents optionally substituted lower alkyl or optionally substituted amino,

V^1 is hydrogen or nitro;

Z is hydrogen or lower alkoxy;

R^1 is lower alkyl or cyano lower alkyl;

A and A^1 each independently represent lower alkylene; and

X^1 is cyano, lower alkoxy, lower alkoxy lower alkoxy, lower alkoxy lower alkoxy lower alkoxy, chlorine, bromine, lower alkoxycarbonyl, lower alkylcarbonyl, optionally substituted phenoxycarbonyl, optionally substituted phenylcarbonyl, optionally substituted phenoxy, hydroxymethyl or lower alkyl carbonyloxymethyl.

2. Disperse monoazo dyestuffs as claimed in Claim 1 wherein A and A^1 each represent ethylene.

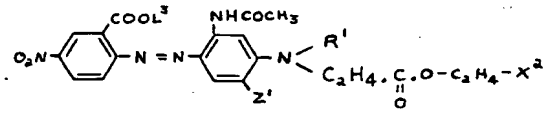
3. Disperse monoazo dyestuffs as claimed in Claim 1 or Claim 2 wherein R^1 is β-cyanoethyl.

4. Disperse monoazo dyestuffs as claimed in any one of the preceding claims wherein L^1 and L^2 are lower alkyl.

5. Disperse monoazo dyestuffs as claimed in Claim 4 wherein L^2 is methyl.

6. Disperse monoazo dyestuffs as claimed in any one of the preceding claims wherein X^1 is cyano, lower alkoxy, lower alkoxy lower alkoxy, lower alkoxycarbonyl, lower alkylcarbonyl, hydroxymethyl or lower alkylcarbonyloxymethyl.

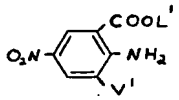
7. Disperse monoazo dyestuffs as claimed in Claim 1 of the formula:



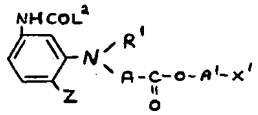
wherein R^1 is as defined in Claim 1, L^3 is lower alkyl, Z^1 is hydrogen or methoxy and X^2 is cyano, lower alkoxy, lower alkoxy lower alkoxy, lower alkoxycarbonyl, lower alkylcarbonyl, hydroxymethyl or lower alkylcarbonyloxy methyl.

8. Disperse monoazo dyestuffs according to Claim 1 as hereinbefore described with reference to any one of Examples 1 to 70.

9. Process for the manufacture of disperse monoazo dyestuffs as claimed in Claim 1 which comprises diazotising an amine of the formula:—



and coupling the resulting diazo compound with a coupling component of the formula:



wherein A, A^1, L^1, L^2, R^1, V^1, X^1 and Z as defined in Claim 1.

10. Process as claimed in Claim 9 as hereinbefore described with reference to any one of Examples 1 to 70.

11. Process for the colouration of synthetic textile materials which comprises applying a dyestuff as claimed in Claim 1 by an aqueous dyeing, padding or printing process.

12. Process as claimed in Claim 11 wherein the synthetic textile material is an aromatic polyester textile material.

13. Process as claimed in Claim 12 wherein the coloured material is subsequently treated with an aqueous solution of an alkali of pH from 8 to 12.

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